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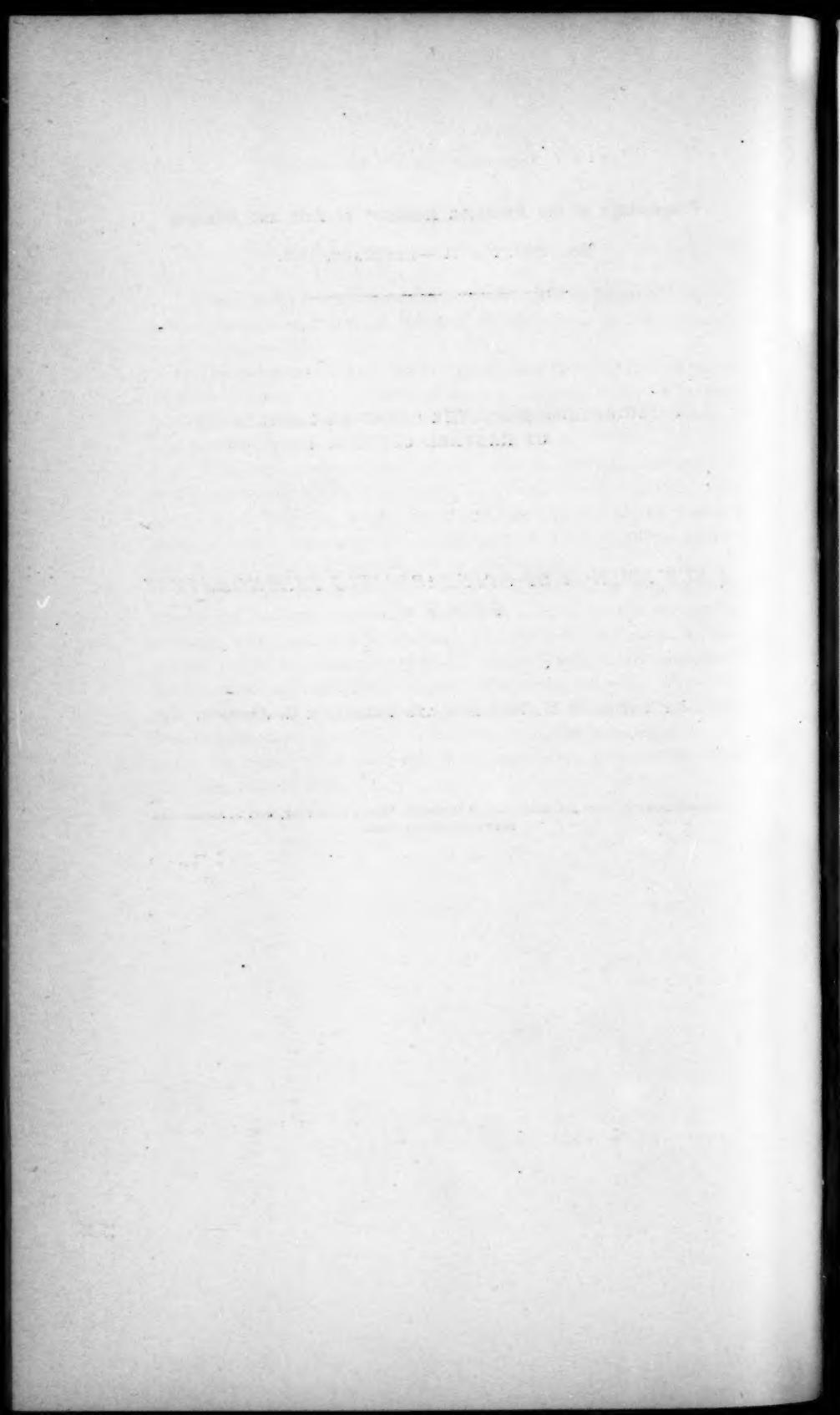
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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY  
OF HARVARD COLLEGE.

*A NEW METHOD OF STANDARDIZING THERMOMETERS  
BELOW 0° C.*

BY THEODORE W. RICHARDS AND FREDERICK G. JACKSON.

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A NEW METHOD OF STANDARDIZING THERMOMETERS  
BELOW 0° C.

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WITHIN recent years the theory of physical chemistry has been profoundly influenced by inferences drawn from the freezing points of aqueous solutions, and many experimenters have contributed data upon this subject. Too often, however, the data are of uncertain value, even when all conceivable precautions have been taken to avoid supercooling and superheating. One cause of the uncertainty is the lack of knowledge concerning the calibration of the thermometers used. Obviously the error of the hundredth of a degree in the thermometer will affect the result by a whole per cent if the fall of temperature caused by the dissolved substance is a degree; and such errors are common. The importance of a simple method of calibrating thermometers below the freezing point of water, both for the theory and practice of physical chemistry, is therefore very apparent. The object of the present paper is to describe the practical working of a method which may be easily carried out by any one, a method which has already been suggested by one of us in a previous paper.<sup>1</sup>

Evidently a solution of given concentration of a given substance must freeze always at exactly a given temperature. If, then, the freezing points of a series of solutions of this substance are determined once for all on a given thermometer of known precision, any other thermometer in any part of the world may be compared at these points with the standard thermometer by finding its readings in similar freezing solutions. If the indications of the standard thermometer are plotted in a curve comparing concentration with scale reading, any point on any thermometer may be

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<sup>1</sup> T. W. Richards, "The Freezing Points of Dilute Solutions," *Journ. Am. Chem. Soc.*, **25**, 297 (1903); *Zeit. phys. Chem.*, **44**, 570 (1903).

verified. This verification is obviously accomplished by immersing the instrument into a mixture of cracked ice and water and adding the dissolved substance until the desired point is reached and maintained. An analytical determination of the concentration of the solution then gives at once by comparison with the standard curve the true value of the temperature which corresponds with this concentration, and hence the error of the thermometer. For example, supposing that the error of the graduation of an uncertain thermometer at reading  $-1.513^{\circ}$  is desired, the thermometer is immersed in ice and water, and hydrochloric acid is added until this point is reached. The solution is then analyzed and found to be  $0.4085^{\circ}$  normal. From the standard curve given below it is quickly found that this concentration should give a reading of  $1.498^{\circ}$ , therefore the thermometer at this place was clearly  $0.015^{\circ}$  in error. The practical value of the method obviously depends wholly upon the accuracy with which the curve comparing concentration and temperature reading has been determined. This accuracy depends, first, on the accuracy of the standard thermometer; second, upon the care in adjusting of the freezing point; and third, on the accuracy of the analysis.

The thermometer used in the present investigation was one carefully standardized by the Bureau International des Poids et des Mesures in Sèvres for this express purpose. It was made by Baudin, and is numbered 15275. Its scale reads as far as  $12^{\circ}$  below zero. Because our results depend upon this single thermometer, they must be considered as only preliminary, for, no matter how careful the calibration, the results of a single thermometer are somewhat uncertain. Nevertheless this thermometer is undoubtedly so much better than those usually used that our results have practical value, even although they cannot be considered as quite the final ones. In the near future we shall hope to take this matter up again with several similar thermometers, obtaining an average value which will be more nearly certain than the present one.

With regard to the care in adjusting the freezing point, it is enough to say here that all reasonable precautions were used. Two series of determinations were conducted: one in a tall beaker, air-jacketed with another beaker, which was in turn surrounded by a mixture of ice and solution of almost exactly the same temperature as the mixture within the inner beaker. The other series was conducted in a large Dewar silvered vacuum jacketed tube, about ten centimeters in internal diameter and thirty centimeters long. This was the more convenient form of apparatus. These two series gave essentially the same results. The thermometer was left in ice for twenty-four hours in every case before it

was used, and was read by means of a powerful micrometer telescope with all the precautions used in the most precise thermometry. Hydrochloric acid was the substance chosen for the solution because its concentration may be determined with accuracy and convenience in many ways.

The third consideration determining the accuracy of the curve is that just referred to, namely, the accuracy of the analysis. While evidently for most purposes volumetric work would give the result quite certainly enough, we nevertheless in the present case preferred to use the gravimetric method of precipitating the hydrochloric acid with an excess of silver nitrate. The solution was drawn from the neighborhood of the thermometer bulb, after thorough stirring, by means of a chilled pipette, whose capacity had been determined by careful calibration. The solution was measured instantly, while it was still cold, and the precipitation of the silver chloride was conducted in the usual manner. In the calculation of the results, the concentrations were computed in terms both of weight of silver chloride from ten cubic centimeters of solution, and in terms of the normality of the hydrochloric acid solution (i. e. the number of gram equivalents per liter calculated from the true volume corrected for the contraction of the glass tube at the temperature of the cold bath). The results were as follows:

#### FREEZING POINTS OF HYDROCHLORIC ACID SOLUTIONS.

Depression of Freezing Point <i>t</i> <sup>o</sup>	Weight of Silver Chloride from 10.00 Cubic Centimeters of Cold Solution. grams.	Normality of Solution <i>c.</i>	<i>t</i> <i>c</i>
0.500 <sup>o</sup>	0.199	0.139	3.59
1.000 <sup>o</sup>	0.397	0.277	3.61
1.500 <sup>o</sup>	0.587	0.409	3.67
2.000 <sup>o</sup>	0.772	0.538	3.72
2.500 <sup>o</sup>	0.951	0.663	3.77
3.000 <sup>o</sup>	1.109	0.773	3.88
3.500 <sup>o</sup>	1.271	0.886	3.95
4.000 <sup>o</sup>	1.430	0.997	4.01

The curve deviates slightly from a straight line, in such a direction that more concentrated solutions produce a slightly greater depression in pro-

portion to their concentration than the less concentrated ones. This is shown by the increasing values in the last column. The hypothesis of ionization predicts the opposite effect.<sup>2</sup>

From these points a curve may be drawn which will enable any one to correct his own thermometer at any point upon repeating the experiments in question.

It may be noted in conclusion that this means of calibrating thermometers is theoretically as exact as any other. According to the Phase Rule, in a system composed of two components, hydrochloric acid and water, four conditions must be fixed in order to fix a point. In the present case the four conditions are the pressure, the concentration of the dissolved substance, and the co-existence in equilibrium of two phases, solution and pure ice.

#### SUMMARY.

This paper describes a simple method of calibrating thermometers at temperatures below the freezing point of water by using as standards of comparison the depressions of the freezing point caused by given additions of hydrochloric acid. The data given are for the construction of a curve enabling direct comparisons of a thermometer to be made with a minimum of labor. The method is shown to be both practically and theoretically satisfactory. This paper is preliminary in nature, and does not pretend to give final values, because only a single standardized thermometer was used.

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<sup>2</sup> It is needless to call attention to the fact that many other cases of this kind have been studied in detail by de Coppel, Büdorff, and others, especially in very recent times by Harry C. Jones.

